TITLE OF THE INVENTION

NEGATIVE ELECTRODE ACTIVE MATERIAL FOR NONAQUEOUS
ELECTROLYTE SECONDARY BATTERY AND NONAQUEOUS
ELECTROLYTE SECONDARY BATTERY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the
benefit of priority from the prior Japanese Patent
Application No. 2002-280303, filed September 26, 2002,
the entire contents of which are incorporated herein by
reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a negative
electrode active material for nonaqueous electrolyte
secondary battery and a nonaqueous electrolyte
secondary battery.

2. Description of the Related Art

Owing to the rapid progress in downsizing
technology of electronic appliances, recently, various
portable electronic appliances are developed and
distributed widely. Downsizing is also required in the
batteries used as power sources for these portable
electronic appliances, and nonaqueous electrolyte
secondary batteries having a high energy density are
attracting much attention.

A nonaqueous electrolyte secondary battery using
metal lithium as negative electrode active material has

a very high energy density, but the battery life is short because dendritic crystals called dendrites deposit on the negative electrode at the time of charging. Besides, in the secondary battery, dendrites

5   grow and reach up to the positive electrode to cause internal short-circuit, thereby leading to safety problems. Accordingly, as a negative electrode active material replacing the lithium metal, it has been proposed to use carbon materials, in particular,

10 graphitized material capable of absorbing and desorbing lithium. However, the capacity of graphitized material is small as compared with that of lithium metal or lithium alloy, and large current characteristics are low. It has been also attempted to use substances of

15 larger lithium absorption capacity and high density, such as elements which are alloyed with lithium, for example, silicon and tin, or an amorphous chalcogen compound.

Above all, silicon can absorb lithium up to a

20 ratio of 4.4 atoms of lithium per 1 atom of silicon, and the negative electrode capacity per weight is about 10 times that of graphitized material. However, since silicon is large in change of volume due to intercalation and deintercalation of lithium in the

25 charging and discharging cycles, particles of the active material are finely pulverized, and there were problems in cycle life.

Jpn. Pat. Appln. KOKAI Publication No. 2000-215887 discloses a negative electrode material for lithium secondary battery, comprising a silicon particle nucleus and a carbon layer for covering the surface of the silicon particle nucleus.

According to the publication, the average particle size of silicon particle nucleus is 0.1 to 50 µm. However, if the average particle size of particle nucleus is 0.1 µm or more, it is hard to prevent pulverization and cracking of the active material in the charging and discharging cycle.

The publication does not specify the half width of any diffraction peak at the (220) plane of silicon, determined by the powder X-ray diffraction of negative electrode material. However, in the publication, as silicon particle nucleus, reagent first class silicon powder by Wako Pure Chemical Industries, Ltd. is used. It is known that this powder is crystalline silicon powder. From the description about the material and in view of FIG. 1 of the publication, it can be inferred that the diffraction peak at the (220) plane of silicon has a half width of less than 0.1°.

FIG. 1 of the publication shows the XRD profile of the negative electrode material used in Example 2. FIG. 1 does not represent the entire image of the peak at the (220) plane of silicon. An accurate half width cannot be determined from FIG. 1. Assuming that the

maximum peak intensity shown on the axis of ordinates in FIG. 1 is the peak intensity of (220) plane, the present inventors measured the half width. The result was a value smaller than 0.1°.

In the negative electrode active material mentioned in the publication, it is difficult to realize a battery of higher capacity and higher cycle characteristic.

BRIEF SUMMARY OF THE INVENTION

It is hence an object of the invention to provide a negative electrode active material for nonaqueous electrode secondary battery capable of achieving high capacity and high cycle characteristic, and a nonaqueous electrolyte secondary battery comprising the negative electrode active material.

According to a first aspect of the invention, there is provided a nonaqueous electrolyte secondary battery comprising:

a positive electrode;

a negative electrode containing a negative electrode active material including carbonaceous particles and a Si phase dispersed in the carbonaceous particles; and

a nonaqueous electrolyte;

wherein the negative electrode active material is 1.5° or more and 8° or less in a half width of a diffraction peak derived from (220) plane of silicon

in powder X-ray diffraction, and

an average size of the Si phase is less than 100 nm.

According to a second aspect of the invention,
5   there is provided a negative electrode active material
for nonaqueous electrolyte secondary battery, including
carbonaceous particles and a Si phase dispersed in the
carbonaceous particles,

wherein a half width of a diffraction peak of
10   (220) plane in powder X-ray diffraction is 1.5° or more
and 8° or less, and

an average size of the Si phase is less than
100 nm.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING
15   FIG. 1 is a partial sectional view showing
a cylindrical nonaqueous electrolyte secondary battery
as an example of a nonaqueous electrolyte secondary
battery according to the invention.

FIG. 2 is a characteristic diagram for comparing
20   a powder X-ray diffraction pattern of a negative
electrode active material and a powder X-ray
diffraction pattern of a raw material in Example 7.

FIG. 3 is a characteristic diagram for comparing
the powder X-ray diffraction pattern of the negative
25   electrode active material and a powder X-ray
diffraction pattern of silicon in Example 7.

FIG. 4 is a characteristic diagram showing

a result of peak separation of the powder X-ray diffraction pattern of the negative electrode active material in Example 7.

FIG. 5 is a transmission electron microscopic picture magnified by 800,000 times of the negative electrode active material in Example 7.

FIG. 6 shows the transmission electron microscopic picture in FIG. 5 with a caption added thereto.

FIG. 7 is image data showing an electron beam diffraction pattern of the negative electrode active material in Example 7.

FIG. 8 shows the image data in FIG. 7 with a caption added thereto.

FIG. 9 is a transmission electron microscopic picture of a lattice image magnified by 4,800,000 times, of the negative electrode active material in Example 7.

FIG. 10 shows the transmission electron microscopic picture in FIG. 9 with a caption added thereto.

FIG. 11 is a transmission electron microscopic picture magnified by 220,000 times of the negative electrode active material in Example 7.

DETAILED DESCRIPTION OF THE INVENTION

A negative electrode active material for nonaqueous electrolyte secondary battery of the invention will be described below.

The negative electrode active material for nonaqueous electrolyte secondary battery according to the invention comprises carbonaceous particles and a Si phase dispersed in the carbonaceous particles, and the half width of the diffraction peak of (220) plane in powder X-ray diffraction is 1.5° or more and 8° or less, and the average size of the Si phase is less than 100 nm. Carbonaceous particles are mother phase for the Si phase. Carbonaceous particles in which a Si phase is dispersed are not a mere mixture of silicon and carbonaceous material, but are a composite material containing Si and C.

As a result of intensive repeated experiments, the inventors discovered that the cycle characteristic can be improved only slightly if attempted to improve by dispersing Si in the carbonaceous material of the negative electrode active material. Concerning its cause, a causative relation is discovered between the size of dispersing crystals of Si and bonding strength with the substrate around Si, and it is found that the higher capacity and enhanced cycle characteristic can be achieved by dispersing microcrystalline Si in the carbonaceous material in a state being included or held in SiO_2 capable of bonding the microcrystalline Si firmly, and thereby the invention is completed.

A preferred aspect of the negative electrode active material of the invention includes three phases,

that is, a Si phase, a SiO_2 phase, and a carbonaceous material phase, and they are compounded in a small size. Since the Si phase can intercalate and deintercalate a large amount of lithium, the capacity of the negative electrode active material can be notably increased. Expansion and shrinkage by intercalation and deintercalation of a large amount of lithium in the Si phase can be lessened by dispersing the Si phase in the other two phases to prevent pulverization of carbonaceous particles, and the carbonaceous material phase can maintain a high conductivity as the negative electrode active material. On the other hand, the SiO_2 phase is strongly bond with the Si phase, and functions as a buffer for preventing pulverization of Si phase, so that it contributes greatly to maintenance of the particle structure.

The ratio of the Si phase, SiO_2 phase, and carbonaceous material phase is preferably in a range of $0.2 \leq (Si/C) \leq 2$ as the molar ratio of Si and carbon. As the quantitative relation between the Si phase and the SiO_2 phase, the molar ratio is preferred to be in a range of $0.6 \leq (Si/SiO_2) \leq 1.5$ because a large capacity and a favorable cycle characteristic can be obtained as the negative electrode active material.

Preferably, the Si phase is dispersed in the carbonaceous particles in a smaller size in order to relax the stress because expansion and shrinkage are

large when intercalating and deintercalating the lithium. Specifically, it is preferred to be dispersed in a cluster size of several units of nm to 300 nm or less at most. The average size of the Si phase is more preferably less than 100 nm. This is because volume changes due to expansion and shrinkage of the Si phase increase as the Si phase size increases, so that, when the average size of the Si phase is 100 nm or more, the negative electrode active material gradually decays along with the progress of charging and discharging, and the charging and discharging cycle of the secondary battery becomes shorter.

The lower limit of the average size of the Si phase is preferred to be 1 nm. The reason is as follows. If the average size of the Si phase is smaller than 1 nm, the rate of Si atoms occupying the crystal surface area increases in the Si phase. Since the Si atoms on the outermost layer of the Si phase form bonds with other different atoms such as oxygen, and do not contribute to intercalation of lithium, if the size of the Si phase is smaller than 1 nm, it is possible that the lithium intercalation amount may decrease significantly.

A more preferred range of the average size of the Si phase is 2 nm or more and 50 nm or less.

Carbonaceous particles may further contain a silicon oxide phase. The silicon oxide phase can

absorb and lessen the expansion and shrinkage due to intercalation and deintercalation of lithium by the Si phase. Preferably, the silicon oxide phase should contain at least one compound of SiO_2 and SiO.

5   The silicon oxide phase such as SiO_2 phase may be either amorphous phase or crystalline phase. The silicon oxide phase such as SiO_2 phase is preferred to be bonded with the Si phase, and dispersed uniformly among carbonaceous particles in a state including or

10   holding the Si phase. Specifically, when at least part of the Si phase is enclosed by silicon oxide phase, expansion and shrinkage of the Si phase can be absorbed by the silicon oxide phase, and the charging and discharging cycle life of the secondary battery can be

15   further extended. Meanwhile, part of the silicon oxide phase may be an isolated phase which does not contact with the Si phase.

        Examples of the carbonaceous material include graphite, hard carbon, soft carbon, amorphous carbon,

20   and acetylene black. One or two or more types of the carbonaceous material may be used. Preferably, a mixture of hard carbon or soft carbon with graphite should be used as the carbonaceous material. Graphite is preferred from the viewpoint of enhancement of

25   conductivity of the active material. On the other hand, hard carbon or soft carbon can coat the Si phase, and is hence large in effect of lessening the expansion

and shrinkage. The carbonaceous material is preferred to be in a form of including the Si phase or the silicon oxide phase such as SiO_2 phase. Specifically, when the Si phase and silicon oxide phase are

5   surrounded with the carbonaceous material phase, expansion and shrinkage of the Si phase can be sufficiently lessened by absorption of the carbonaceous material phase and silicon oxide phase, so that the charging and discharging cycle of the secondary battery

10 can be further enhanced.

The shape of the carbonaceous particles is not particularly specified, and may include, for example, spherical, fibrous, scaly and indefinite shapes.

The average particle size of carbonaceous

15 particles is preferred to be 5 μm or more and 100 μm or less. The specific surface area of carbonaceous particles is preferred to be 0.5 m^2/g or more and 15 m^2/g or less. The particle size and specific surface area of active material particles have an

20 effect on the reaction speed of intercalation and deintercalation of lithium, and hence have a large influence on the negative electrode characteristics. By defining the average particle size and specific surface area of carbonaceous particles in the specified

25 range, the secondary battery can exhibit the characteristics stably.

The average particle size of carbonaceous

particles can be measured, for example, by laser diffraction particle size analyzer.

The negative electrode active material is 1.5° or more to 8° or less in the half width of the diffraction peak derived from (220) plane of silicon in powder X-ray diffraction. This is due to the reason explained below. The half width of the diffraction peak of Si (220) plane becomes smaller as the crystal grains of the Si phase grow, and the active material particles are likely to be cracked by expansion and shrinkage due to intercalation and deintercalation of lithium as the crystal grains of the Si phase become larger. If the half width is less than 1.5°, expansion and shrinkage due to intercalation and deintercalation of lithium of the Si phase increase. Therefore, pulverization of carbonaceous particles is promoted, and the charging and discharging cycle life of the secondary battery becomes shorter. On the other hand, if the half width exceeds 8°, the Si phase is high in amorphous property, and chemical stability of the Si phase is lower, so that decomposition reaction of nonaqueous electrolyte is likely to occur, and hence the discharge capacity or charging and discharging cycle life of the secondary battery is lowered. A more preferred range of the half width is 2° or more and 6° or less.

Carbonaceous particles are preferred to satisfy the following formula (1):

$$0.2 \leq (X_1/X_2) \leq 2 \qquad\qquad (1)$$

where the X_1 is the molar number of a silicon atom in the carbonaceous particles, and the X_2 is the molar number of a carbon atom in the carbonaceous particles.

5　When the silicon oxide phase is contained in the carbonaceous particles, meanwhile, the molar number of silicon atom X_1 is the total molar number of silicon atom composing the Si phase and silicon atom composing the silicon oxide phase.

10　The reason for defining (X_1/X_2) in this range is explained. If (X_1/X_2) is less than 0.2, high capacity may not be obtained in the secondary battery. On the other hand, if (X_1/X_2) exceeds 2, expansion and shrinkage of the Si phase may not be absorbed

15　sufficiently. Therefore, distortion due to expansion and shrinkage is increased, pulverization of carbonaceous particles is promoted, and a long charging and discharging cycle life may not be obtained in the secondary battery.

20　Carbonaceous particles are preferred to satisfy the following formula (2):

$$0.6 \leq (X_1/X_3) \leq 1.5 \qquad\qquad (2)$$

where the X_1 is the molar number of a silicon atom of the Si phase, and the X_3 is the molar number of a

25　silicon oxide molecule of the silicon oxide phase.

The reason for defining (X_1/X_3) in this range is explained. Since the silicon oxide does not

intercalate or deintercalate lithium, if (X_1/X_3) is less than 0.6, high capacity may not be obtained in the secondary battery. On the other hand, if (X_1/X_3) exceeds 2, expansion and shrinkage of Si phase may not be absorbed sufficiently. Therefore, distortion due to expansion and shrinkage is increased, pulverization of carbonaceous particles is promoted, and a long charging and discharging cycle life may not be obtained in the secondary battery.

First and second methods of manufacturing a negative electrode active material for nonaqueous electrolyte secondary battery of the invention are explained below.

The first method of manufacturing a negative electrode active material for nonaqueous electrolyte secondary battery of the invention includes baking a mixture containing at least one organic material of a carbon material and a carbon material precursor, and SiO_X ($0.8 \leq X \leq 1.5$), in an inert atmosphere at temperature of 850°C or more and less than 1400°C.

The second method of manufacturing a negative electrode active material for nonaqueous electrolyte secondary battery of the invention includes treating a mixture containing at least one organic material of a carbon material and a carbon material precursor, and SiO_X ($0.8 \leq X \leq 1.5$), by dynamic compounding process in an inert atmosphere.

According to the first and second manufacturing methods, the negative electrode active material of the invention can be obtained.

To begin with, the first manufacturing method is explained.

As the Si material, it is preferred to use SiO_X ($0.8 \leq X \leq 1.5$). In particular, it is preferred to use SiO ($x \approx 1$) for keeping the quantitative relation of Si phase and SiO_2 phase at a favorable ratio. The form is powder and the average particle size is 1 μm or more and 50 μm or less. In a baking process explained later, SiO_X is separated into a fine Si phase and SiO_2 phase, and in order to assure a conductive path between fine separated Si phases, the average particle size of SiO_X powder is preferred to be as small as possible. This is because, if the average particle size is large, the Si phase is thickly coated with the SiO_2 phase of insulator in the central parts of particles, and the reaction of intercalation and deintercalation of lithium in the active material is impeded. Therefore, the average particle size of SiO_X powder is preferred to be 50 μm or less. However, since the surface of SiO_X particles contacting with the atmosphere is likely to be oxidized to become SiO_2, when the average particle size is extremely small, the surface area increases, so that the particle surface becomes SiO_2, and the composition thereof becomes unstable.

Accordingly, the average particle size is preferred to be 1 μm or more.

As raw materials of the carbonaceous material, in addition to carbon materials which is carbonized or graphitized such as graphite, acetylene black, carbon black, and hard carbon, carbon material precursors such as pitch, resin and polymer, which become the carbon material by being heated in an inert atmosphere can be used. As materials of the carbonaceous material, combining a carbon material having high electric conductivity such as graphite and acetylene black, and a carbon material precursor which is not carbonized yet such as polymer and pitch is preferred. When the carbon material precursor such as pitch and polymer is fused or polymerized with SiO_X powder in a stage before baking, SiO_X particles can be dispersed in the carbon material precursor. In the manufacturing method of the invention, the carbonizing and baking temperature is relatively low, that is, 800°C or more and less than 1400°C, the degree of graphitization of carbonized pitch or polymer is not so high. Therefore, in order to enhance the conductivity of the active material, it is preferred to add graphite, acetylene black, or the like.

When pitch is used as the carbon material precursor, SiO_X and the carbon materials such as graphite are added in fused pitch, and they are mixed,

cooled, solidified, and then ground, and after the surface thereof is oxidized and made infusible, the resultant material is subject to carbonization baking. When polymer is used as the carbon material precursor,

5   SiO_X and the carbon material such as graphite are dispersed in monomer, and polymerized and solidified, and the resultant material is subject to carbonization baking.

The carbonization baking process is executed in an

10   inert atmosphere of Ar gas or the like. In carbonization baking process, polymer or pitch is carbonized, and SiO_X is separated into a Si phase and a SiO_2 phase by disproportionation reaction. In case of x = 1, the reaction is expressed in the following

15   formula (A):

$$2SiO \rightarrow Si + SiO_2 \qquad\qquad (A)$$

This disproportionation reaction progresses at a higher temperature than 800°C. SiO_X is separated into a fine Si phase and SiO_2 phase due to

20   disproportionation reaction. As the reaction temperature becomes higher, the crystal size of the Si phase becomes larger, and the half width of peak of Si (220) plane becomes smaller. The baking temperature at which a preferred half width is obtained is in a range

25   of 850°C to less than 1400°C. Further, the Si produced by disproportionation reaction reacts with carbon at a temperature higher than 1400°C, and is transformed

into SiC. Since SiC is completely inert to intercalation of lithium, the capacity of the active material drops when SiC is formed. Therefore, the temperature of carbonization baking is preferred to be

5   850°C or more and less than 1400°C, and more preferably 850°C or more and 1300°C or less, and still more preferably 900°C or more and 1100°C or less. The baking time is preferred to be somewhere between about 1 hour and 12 hours.

10   The negative electrode active material of the invention is obtained by this synthesizing method. The product after carbonization baking is provided as an active material after adjustment of the particle size, specific surface area and the like by means of various

15   mills, a pulverizing machine, a grinder, or the like.

The second method of manufacturing a negative electrode active material of the invention is described below.

Dynamic compounding process is executed by means

20   of turbo mill, ball mill, mechanofusion, disk mill, etc.

As a Si material, it is preferred to use SiO_X ($0.8 \leq X \leq 1.5$). It is particularly preferred to use SiO ($X \approx 1$) from the viewpoint of obtaining a favorable

25   ratio of quantitative relation between the Si phase and the SiO_2 phase. The form of SiO_X may be bulk, but fine powder is preferred for shortening the processing time,

and the average particle size is preferred to be 0.5 μm
or more and 100 μm or less. This is owing to the
reason explained below. If the average particle size
exceeds 100 μm, the Si phase is thickly coated with the

5 SiO_2 phase of an insulator in the central area of
particles, and the reaction of intercalation and
deintercalation of lithium in the active material may
be impeded. On the other hand, if the average particle
size is less than 0.5 μm, the surface area is large, so

10 that the particle surface becomes SiO_2, and the
composition thereof may be unstable.

As an organic material, at least one may be
selected from a carbon material and a carbon material
precursor. Examples of the carbon material include

15 graphite and coke. On the other hand, examples of the
carbon material precursor include low temperature
baking coal and pitch. In particular, since
materials, such as pitch, which are fused by heating
are fused in the mill process and disturb the progress

20 of compounding, adding nonfusible materials such as
coke and graphite is preferred.

The operating condition of compounding process
varies according to the device, but it is preferred to
operate in a condition allowing a sufficient progress

25 of grinding and compounding. However, if the output is
raised excessively or too much time is taken in the
compounding process, Si and C react with each other to

produce SiC which is inert to Li intercalation reaction. Accordingly, the processing condition is preferably determined properly so as to promote grinding and compound sufficiently, but not to induce SiC production.

The baking process may be executed in the same condition as explained in the first manufacturing method.

The nonaqueous electrolyte secondary battery using the negative electrode active material of the invention is described below.

1) Positive electrode

The positive electrode has a structure in which a positive electrode active material layer containing an active material is carried on one side or both sides of a positive electrode current collector.

The thickness of one side of the positive electrode active material layer is preferred to be in a range of 10 μm to 150 μm from the viewpoint of large current discharging characteristic and cycle life of the battery. Therefore, when carried on both sides of the positive electrode current collector, the total thickness of the positive electrode active material layer is preferred to be in a range of 20 μm to 300 μm. A more preferred range of the thickness of one side is 30 μm to 120 μm. Within this range, the large current discharging characteristic and the cycle life can be

enhanced.

The positive electrode active material layer may also contain a conductive agent aside from the positive electrode active material.

The positive electrode active material layer may further contain a binding agent for binding the positive electrode materials.

The positive electrode active material may be selected from various oxides, and in order to obtain a high voltage, it is preferred to use, for example, manganese dioxide, lithium manganese composite oxide, lithium-containing nickel cobalt oxide (for example, $LiCoO_2$), lithium-containing nickel cobalt oxide (for example, $LiNi_{0.8}Co_{0.2}O_2$), and lithium manganese composite oxide (for example, $LiMn_2O_4$, and $LiMnO_2$).

Examples of the conductive agent include acetylene black, carbon black, and graphite.

Specific examples of the binding agent include polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), ethylene-propylene-diene copolymer (EPDM), and styrene-butadiene rubber (SBR).

The blending rate of the positive electrode active material, conductive agent, and binding agent is in a range of 80 to 95 wt.% of the positive electrode active material, 3 to 20 wt.% of the conductive agent, and 2 to 7 wt.% of the binding agent, so that favorable large current discharging characteristic and cycle life can

be obtained.

As the current collector, a conductive substrate of a porous structure or non-porous conductive substrate may be used. The thickness of the current collector is preferred to be 5 to 20 μm. In this range, the electrode strength and reduction of weight are balanced favorably.

2) Negative electrode

The negative electrode has a structure in which a negative electrode active material layer containing a negative electrode active material is carried on one side or both sides of a negative electrode current collector.

The thickness of the negative electrode active material layer is preferred to be in a range of 10 μm to 150 μm. Therefore, when carried on both sides of the negative electrode current collector, the total thickness of the negative electrode active material layer is preferred to be in a range of 20 μm to 300 μm. A more preferred range of the thickness of one side is 30 μm to 100 μm. Within this range, the large current discharging characteristic and the cycle life can be enhanced.

The negative electrode active material layer may also contain a binding agent for binding the negative electrode materials. Specific examples of the binding agent include polytetrafluoroethylene (PTFE),

polyvinylidene fluoride (PVdF), ethylene-propylene-
diene copolymer (EPDM), and styrene-butadiene rubber
(SBR).

The negative electrode active material layer may
further contain a conductive agent. Examples of the
conductive agent include acetylene black, carbon black,
and graphite.

As the current collector, a conductive substrate
of porous structure or non-porous conductive substrate
may be used. The conductive substrates may be made
from, for example, copper, stainless steel or nickel.
The thickness of the current collector is preferred to
be 5 to 20 μm. In this range, the electrode strength
and reduction of weight are balanced favorably.

3) Electrolyte

Examples of the electrolyte include nonaqueous
electrolysis solution, electrolyte-impregnated polymer
electrolyte, polymer electrolyte, and inorganic solid
electrolyte.

The nonaqueous electrolysis solution is prepared
by dissolving an electrolyte in a nonaqueous solvent,
and it is held among gaps in the electrode group in a
liquid form.

The nonaqueous solvent is preferred to be a mixed
solvent of propylene carbonate (PC) or ethylene
carbonate (EC) with a nonaqueous solvent having lower
viscosity than PC or EC (hereinafter called second

solvent).

As the second solvent, for example, chain carbon is preferred, and other preferred examples include dimethyl carbonate (DMC), methyl ethyl carbonate (MEC), diethyl carbonate (DEC), ethyl propionate, methyl propionate, γ-butyrolactone (BL), acetonitrile (AN), ethyl acetate (EA), toluene, xylene, and methyl acetate (MA). These second solvents may be used either alone or as a mixture of two or more solvents. In particular, the second solvent is preferred to have the number of donors of 16.5 or less.

The viscosity of the second solvent is preferred to be 2.8 cmp or less at 25°C. The content of ethylene carbonate or propylene carbonate in the mixed solvent is preferred to be in a range of 10% to 80% as the ratio by volume. A more preferred range of content of ethylene carbonate or propylene carbonate is 20% to 75% as the ratio by volume.

Examples of the electrolyte contained in the nonaqueous electrolysis solution include lithium salts such as lithium perchlorate ($LiClO_4$), lithium phosphate hexafluoride ($LiPF_6$), lithium borate tetrafluoride ($LiBF_4$), lithium arsenate hexafluoride ($LiAsF_6$), lithium trifluoromethasulfonate ($LiCF_3SO_3$), and bistrifluoromethyl sulfonyl imide lithium [$LiN(CF_3SO_2)_2$]. In particular, it is preferred to use $LiPF_6$ or $LiBF_4$.

The amount of electrolyte dissolved in the nonaqueous solvent is preferred to be 0.5 to 2 mol/L.

4) Separator

A separator can be used when using nonaqueous electrolysis solution or electrolyte-impregnated polymer electrolyte. The separator is a porous separator. Materials for the separator include, for example, a porous film containing polyethylene, polypropylene, or polyvinylidene fluoride (PVdF), and a nonwoven cloth made of synthetic resin. Above all, a porous film containing polyethylene or polypropylene or both of them is preferred from the viewpoint of enhancing the safety of the secondary battery.

The thickness of the separator is preferred to be 30 μm or less. If the thickness exceeds 30 μm, the distance between the positive and negative electrodes is too long, and the internal resistance may increase. The lower limit of the thickness is preferred to be 5 μm. If the thickness is less than 5 μm, the strength of the separator is extremely lowered and an internal short-circuit is likely to occur. The upper limit of the thickness is more preferably 25 μm, and the lower limit is more preferably 10 μm.

The thermal shrinkage of the separator when it is kept for 1 hour at 120°C is preferred to be 20% or less. If the thermal shrinkage exceeds 20%, it is highly possible that short-circuit may occur by

heating. More preferably, the thermal shrinkage should be 15% or less.

The porosity of the separator is preferred to be in a range of 30 to 70%. The reason is as follows. If the porosity is less than 30%, it may be difficult to obtain a high electrolyte holding property in the separator. On the other hand, if the porosity exceeds 70%, sufficient separator strength may not be obtained. A more preferable range of the porosity is 35 to 70%.

The air permeability of the separator is preferred to be 500 sec/100 cm^3 or less. If the air permeability exceeds 500 sec/100 cm^3, it may be hard to obtain a high lithium ion mobility in the separator. The lower limit of the air permeability is 30 sec/100 cm^3. If the air permeability is less than 30 sec/100 cm^3, a sufficient separator strength may not be obtained.

The upper limit of the air permeability is more preferably 300 sec/100 cm^3, and the lower limit is more preferably 50 sec/100 cm^3.

As an example of the nonaqueous electrolyte secondary battery of the invention, a cylindrical nonaqueous electrolyte secondary battery is specifically described below while referring to FIG. 1.

For example, a stainless steel container 1 of cylindrical shape with a bottom includes an insulator 2 provided at the bottom thereof. An electrode group 3 is contained in the container 1. The electrode group 3

includes a positive electrode 4, a separator 5, a negative electrode 6, and a separator 5, which are laminated into a band, and wound spirally such that the separator 5 comes to the outer side.

5   The container 1 is filled with an electrolysis solution. An insulating paper 7 having a central opening, is provided above the electrode group 3 in the container 1. An insulating sealing plate 8 is provided in the upper opening of the container 1, and by

10   crimping the upper opening to the inner side, the sealing plate 8 is fixed to the container 1. A positive electrode terminal 9 is fitted to the center of the insulating sealing plate 8. One end of a positive electrode lead 10 is connected to the positive

15   electrode 4, and the other end is connected to the positive electrode terminal 9. The negative electrode 6 is connected to the container 1, as a negative electrode terminal, by way of a negative electrode lead (not shown).

20   FIG. 1 shows an example of application into the cylindrical nonaqueous electrolyte secondary battery, but the invention may be applied in the nonaqueous electrolyte secondary battery of any form. For example, it can be applied in a prismatic nonaqueous

25   electrolyte secondary battery, a thin type nonaqueous electrolyte secondary battery, a coin-shaped nonaqueous electrolyte secondary battery, and the like.

The electrode group contained in the container of the battery is not limited to the spiral shape, but, for example, the positive electrode, separator and negative electrode may be laminated in this sequence in plural layers.

In FIG. 1, the example is an application in the nonaqueous electrolyte secondary battery using a case made of a metal can, but the invention can be similarly applied in a nonaqueous electrolyte secondary battery using a case made of a film material. As the film material, it is preferred to use a laminated film including a thermoplastic resin and an aluminum layer.

Specific examples of the invention are given below, and the effects thereof are explained. It must be noted, however, that the invention is not limited to these examples.

(Examples 1 to 5 and Comparative examples 1 and 2)

As the SiO_x material, amorphous SiO powder having the average particle size of 30 μm was prepared. As the carbon material, graphite having the average particle size of 6 μm was prepared. As the carbon material precursor, furfuryl alcohol was prepared. The blending ratio by weight was SiO: graphite: furfuryl alcohol = 3: 0.5: 5. To furfuryl alcohol, water was added by 1/10 weight, graphite and SiO were added and stirred. Then, dilute hydrochloric acid was added by 1/10 weight of furfuryl alcohol, and stirred, and the

mixture was let stand to be polymerized and solidified.

The obtained solid material was baked in Ar gas at baking temperature and for baking time shown in Table 1, cooled to room temperature, and then ground by 5 a grinder, so that a negative electrode active material was obtained by sifting by 30 μm in particle size.

Table 1

	Baking temperature	Baking time
Example 1	800℃	3 hours
Example 2	1000℃	3 hours
Example 3	1100℃	3 hours
Example 4	1200℃	3 hours
Example 5	1300℃	3 hours
Comparative example 1	700℃	3 hours
Comparative example 2	1400℃	3 hours

10   (Comparative example 3)

Using Si powder having the average particle size of 0.5 μm instead of SiO powder, the Si powder, graphite and furfuryl alcohol were mixed at a ratio by weight of Si: graphite: furfuryl alcohol = 1: 0.5: 5, 15 and a negative electrode active material was obtained in the same manner as in Example 1 except that the baking temperature was 1000°C.

The obtained negative electrode active materials of Examples 1 to 5 and Comparative examples 1 to 3 were 20 tested by powder X-ray diffraction and transmission

electron microscope observation in the following

conditions, and the charging and discharging

characteristics were evaluated in the following method,

and obtained results are shown in Table 2.

5   (Powder X-ray diffraction)

For the obtained powder samples, powder X-ray

diffraction was carried out, and the half width of the

peak of Si (220) plane was measured. It was measured

in the following condition by using an X-ray

10   diffraction measuring apparatus of Mac Science Co.

(model M18XHF22).

Counter cathode: Cu

Tube voltage: 50 kV

Tube current: 300 mA

15   Scanning speed: 1° (2θ)/min

Time constant: 1 sec

Receiving slit: 0.15 mm

Divergent slit: 0.5°

Scattering slit: 0.5°

20   FIG. 2 shows an X-ray diffraction (XRD) pattern of

the negative electrode active material of Example 7 and

an XRD pattern of a raw material of the negative

electrode active material. FIG. 2 shows XRD patterns

of, sequentially from the bottom:

25   (i) material SiO,

(ii) material graphite,

(iii) SiO baked for 3 hours at 1000°C in argon gas

flow,

(iv) XRD pattern of negative electrode active material (sample) of Example 7, and

(v) XRD pattern of 4N silicon.

FIG. 3 shows only the XRD pattern (XRD pattern of sample) of (iv) and the XRD pattern (XRD pattern of 4N silicon) of (v).

As known from (i) of FIG. 2, peak is not observed in the XRD pattern of material SiO, and it is known to be amorphous. As clear from comparison between pattern (iii) and pattern (v), when SiO is baked in an inert atmosphere, a broad Si peak is formed. On the other hand, as understood from XRD pattern (iv), the negative electrode active material of Example 7 is a Si-C composite material having complicated peaks, but basically the diagram shows a compounded peak of the peak derived from material graphite of (ii) and the peak derived from baked SiO of (iii). Hence, the peak appearing near 47° of 2θ in FIGS. 2 and 3 is the diffraction peak of silicon (220) plane.

From the X-ray diffraction pattern, the half width of the peak (° (2θ)) of plane index (220) of Si appearing at spacing d of 1.92 Å (2θ being 47.2°) was measured. If the peak of Si (220) overlaps with the peak of other substances contained in the active material, the peak was isolated and the half width was measured. FIG. 4 shows an example of peak separation.

As known from FIG. 4, plural peaks derived from the graphite structure of the graphite appearing at 2θ of 42 to 46° overlap with the peak (P_{220}) of the Si (220) plane at 2θ of near 47°. By peak separation

5   calculation, each peak was isolated, and the half width of the (220) plane peak of Si was determined (FWHM = 3.005°).

Further, from the results of the X-ray diffraction pattern, it was confirmed that the silicon oxide phase

10   is contained in the negative electrode active materials of Examples 1 to 5.
(Transmission electron microscope (TEM) observation)

A TEM sample was prepared by suspending a small amount of powder in ethanol solution, and dropping the

15   suspension on a collodion membrane. After drying the wet collodion sufficiently, light field image, dark field image and lattice image were observed at magnification of 100,000 to 500,000 times by FE-TEM (field emission transmission electron microscope; model

20   HF-2000) at acceleration voltage of 200 kV. Further, to identify the growth phase, an electron beam diffraction pattern was photographed and the crystal structure of the growth phase was identified.

FIG. 5 shows a transmission electron microscopic

25   picture magnified by 800,000 times of the negative electrode active material in Example 7. FIG. 6 shows the transmission electron microscopic picture in FIG. 5

with a caption added thereto. FIG. 7 is image data

showing electron beam diffraction pattern of the

negative electrode active material in Example 7.

FIG. 8 shows the image data in FIG. 7 with a caption

5   added thereto. FIG. 9 is a transmission electron

microscopic picture of a lattice image magnified by

4,800,000 times of the negative electrode active

material in Example 7. FIG. 10 shows the transmission

electron microscopic picture in FIG. 9 with a caption

10   added thereto.

As can be seen from FIGS. 5 and 6, the negative

electrode active material of Example 7 is a composite

material having multiple fine grains existing in

carbonaceous particles. On the other hand, from the

15   Debye-Scherrer rings of electron beam diffraction

patterns in FIGS. 7 and 8, the patterns derived from

(111) plane, (220) plane and (311) plane of Si were

confirmed, and it is found that the fine grains were

identified to be microcrystals of Si. Also from the

20   lattice image in FIGS. 9 and 10, the Si phase was

confirmed to be microcrystals, and the spacing d of

(111) plane of Si was found to be 0.314 nm.   It has

been also confirmed from FIG. 6 that most Si phase is

surrounded with silicon oxide phase such as SiO_2 phase,

25   and that the silicon oxide phase is surrounded with the

carbonaceous material phase.

The average size of the Si phase was determined in

the method as explained below.

That is, the size was measured in all Si microcrystals observed in TEM photograph (the picture size is 600 nm × 500 nm) taking the dark field image magnified by 400,000 times, and the average size was calculated. Of the TEM photographs used in measurement of the average size, the image of the negative electrode active material of Example 7 is shown in FIG. 11 as an example. FIG. 11 is a copy of the TEM photograph actually used to determine the average size. Note that the copy is reduced in size for presentation on a sheet of limited size and shows Si microcrystals magnified 220,000 times.

The molar ratio (X_1/X_2) of the negative electrode active material in Example 1 was 1.03, and the molar ratio (X_1/X_3) was 0.86.

(Charging and discharging test)

5 wt.% of acetylene black and 3 wt.% of polytetrafluoroethylene were added to the negative electrode active material to be formed in a sheet, and the sheet was compressed to a stainless steel mesh, and then dried in vacuum at 150°C to obtain a test electrode. The counter electrode and reference electrode were made of metal Li. A nonaqueous electrolysis solution was obtained by dissolving 1 M of $LiPF_6$ in a nonaqueous solvent in which ethylene carbonate (EC) and methyl ethyl carbonate (MEC) are

mixed at a ratio by volume of 1:2. Using the obtained test negative electrode, counter electrode, reference electrode and nonaqueous electrolysis solution, a test cell was assembled in an argon atmosphere, and a

5 charging and discharging test was conducted.

The condition of the charging and discharging test is as follows. The battery was charged at a current density of 1 mA/cm^2 up to a potential difference of 0.01 V between the reference electrode and the test

10 electrode, and was further charged at a constant voltage of 0.01 V for 8 hours. It was discharged at a current density of 1 mA/cm^2 until becoming 3 V.

Table 2 shows the discharge capacity of the first cycle in the charging and discharging test, the

15 discharge capacity maintenance rate after 50 cycles (supposing the discharge capacity of the first cycle to be 100%), the half width of the peak of Si (220) plane obtained from the powder X-ray diffraction, and the average size of the Si phase.

Table 2

	Discharge capacity (mAh/g)	Capacity maintenance rate after 50 cycles (%)	Si (220) peak half width (°)	Average size of Si phase (nm)
Example 1	674	91	8.0	4.02
Example 2	688	95	2.6	8.40
Example 3	675	83	2.0	9.67
Example 4	690	88	2.1	14.2
Example 5	640	82	2.0	16.5
Comparative example 1	470	79	No peak	Si phase was not observed
Comparative example 2	320	80	1.2	16.8
Comparative example 3	870	23	0.2	500

As known from the results shown in Table 2, the secondary battery having the negative electrode active material of Examples 1 to 5 has a large discharge capacity and a favorable cycle characteristic. That

5   is, in Comparative example 1, since the baking temperature was 700°C, SiO was not separated into Si and SiO_2, and thereby both the capacity and the cycle characteristic were lowered. In Comparative example 2, since the baking temperature was 1400°C, the half width

10   of the peak of Si (220) plane was smaller and the cycle characteristic was lowered, and also the produced Si reacted with C to be SiC incapable of absorbing Li, so that the capacity dropped significantly. In Comparative example 3, since the crystal size of the Si

15   phase was large, the half width was small, and SiO_2 was absent, so that the cycle characteristic dropped significantly.

(Example 6)

Using a ball mill (model P-5 of Fritsch), the

20   negative electrode active material was synthesized in the material composition, ball mill operating condition, and baking condition as shown in Table 3.

In the case of the ball mill, a stainless steel container of volume of 250 ml and a ball of 10 mm in

25   diameter were used. The sample was charged by 20 g. The material contained 8 g of SiO powder having the average particle size of 45 μm, and 12 g of graphite

powder having the average particle size of 6 μm as the carbon material. The rotating speed (rpm) of the ball mill and the treatment time are shown in Table 3.

The composite material obtained by the ball mill was baked in Ar gas at the baking temperature and for the baking time shown in Table 3, cooled to room temperature, and then ground by a grinder, and a negative electrode active material was obtained by sifting by 30 μm in particle size.

The molar ratio (X_1/X_2) of the negative electrode active material in Example 6 was 0.68, and the molar ratio (X_1/X_3) was 1.12.

(Examples 7 to 17)

Negative electrode active materials were obtained in the same procedure as in Example 6, except that the average particle size and charging amount of SiO, type and charging amount of the organic material, rotating speed of the ball mill, treating time, baking temperature and baking time were set as shown in Table 3. As the carbon material precursor in Table 3, ground pitch of 1 mm in particle size was used.

(Comparative example 4)

A negative electrode active material was obtained in the same procedure as in Example 6, except that Si powder having the average particle size of 1 μm was used instead of SiO powder.

The negative electrode active materials of

Examples 6 to 17 and Comparative example 4 were tested by powder X-ray diffraction and transmission electron microscope observation in the same conditions as in Example 1, and the negative electrode active materials of Examples 6 to 17 were confirmed to be composite materials having multiple Si microcrystal grains existing in carbonaceous particles, and it was also known that silicon oxide phases are contained in the carbonaceous particles. Table 4 shows the half width of the peak of Si (220) plane, average size of the Si microcrystal phase, discharge capacity of first cycle, and capacity maintenance rate after 50 cycles. The charging and discharging characteristic was evaluated in the same condition as explained in Example 1.

Table 3

	Material		Ball mill condition		Baking condition	
	SiO	Organic material	Rotating speed (rpm)	Treating time (hrs)	Baking temperature	Baking time
Example 6	45 μm 8g	Graphite 12g	80	18	1000°C	3h
Example 7	45 μm 8g	Graphite 12g	100	16	1000°C	3h
Example 8	45 μm 8g	Graphite 12g	150	16	1000°C	3h
Example 9	45 μm 8g	Graphite 12g	200	13	1000°C	3h
Example 10	45 μm 12g	Graphite 8g	105	16	1000°C	3h
Example 11	45 μm 10g	Graphite 10g	105	16	1000°C	3h
Example 12	45 μm 6g	Graphite 14g	105	16	1000°C	3h
Example 13	45 μm 8g	Graphite 6g+pitch 6g	125	13	1000°C	3h
Example 14	45 μm 8g	Graphite 2g+pitch 10g	125	14	1000°C	3h
Example 15	45 μm 8g	Graphite 8g+pitch 4g	125	16	1000°C	3h
Example 16	5 μm 8g	Graphite 12g	105	16	1000°C	3h
Example 17	5 μm 8g	Graphite 6g+pitch 6g	105	16	1000°C	3h
Comparative example 4	Si;1 μm;8g	Graphite 12g	80	18	1000°C	3h

Table 4

	Si (220) peak half width (°)	Average size of Si phase (nm)	Discharge capacity (mAh/g)	Capacity maintenance rate after 50 cycles (%)
Example 6	3.04	9.21	920	82
Example 7	3.87	9.49	941	92
Example 8	3.49	7.33	902	94
Example 9	6.02	6.89	751	91
Example 10	2.78	8.60	1121	87
Example 11	3.02	9.19	1005	85
Example 12	3.32	10.03	866	91
Example 13	3.46	8.76	911	92
Example 14	3.33	11.27	896	91
Example 15	3.68	8.54	915	88
Example 16	4.33	7.55	898	92
Example 17	4.53	8.30	899	91
Comparative example 4	0.164	1 μm	1055	15

As clear from Tables 3 and 4, it is understood that the secondary batteries having the negative electrode active materials of Examples 6 to 17 of which half width of the peak of Si (220) plane is 1.5° to 8°, and of which average size of the Si phase is less than 100 nm are excellent in both the discharge capacity and capacity maintenance rate after 50 cycles.

On the contrary, in the secondary battery having the negative electrode active material of Comparative example 4 of which half width of the peak of Si (220) plane is smaller than 1.5°, and of which average size of the Si phase is not less than 100 nm, the capacity maintenance rate after 50 cycles was smaller as compared with Examples 6 to 17.

Negative electrode active materials of Examples 6 to 17 in Table 4 are obtained by the method that includes compounding graphite powder and Si powder by ball mill treatment and then baking. Since the raw material of graphite powder has been already graphitized, it is hardly influenced by heat effects of baking or the like, so that the charging and discharging characteristic of the negative electrode active material of Examples 6 to 17 mainly depends on the state of the Si phase. Therefore, by comparing Examples 6 to 17, it is understood that Examples 6 to 8, and 10 to 17 of which half-width of the peak of Si (220) plane is in a range of 2 to 6° have a higher

discharge capacity as compared with Example 9 of which half-width is greater than 6°.

On the other hand, the negative electrode active materials of Examples 1 to 5 in Table 2 are obtained by the method that includes baking a mixture of a carbon precursor and SiO. As known from Table 2, when a carbon precursor is used as the raw material, secondary batteries excellent in both the discharge capacity and charging and discharging cycle life are obtained by baking at temperature lower than 1100°C as in Examples 1 and 2. When the carbon precursor is used as the material, the state of the Si phase is likely to change depending on the baking condition, and the state of the carbonaceous phase existing around the Si phase is also likely to change. When the baking temperature is 1100°C or more, the production reaction of SiC takes place. As a result, when the carbon precursor is used as the material, by keeping the baking temperature at lower than 1100°C, secondary batteries excellent in both the discharge capacity and charging and discharging cycle life are obtained.

As described herein, the invention can provide a negative electrode active material capable of obtaining a nonaqueous electrolyte secondary battery with large capacity and long cycle life, and a nonaqueous electrolyte secondary battery comprising such negative electrode active material.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments

5   shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.